Tuning the \([L_2\text{Rh} \cdots \text{H}_3\text{B} \cdots \text{NR}_3]^+\) Interaction using Phosphine Bite Angle. Demonstration by the Catalytic Formation of Polyaminoboranes

Romaeo Dallanegra\textsuperscript{a}, Alasdair P. M. Robertson\textsuperscript{b}, Adrian B. Chaplin\textsuperscript{a}, Ian Manners\textsuperscript{b,\*} and Andrew S. Weller\textsuperscript{a,\*}

\textsuperscript{a}Department of Chemistry, Inorganic Research Laboratory, University of Oxford, Oxford, OX1 3QR, UK.

\textsuperscript{b}School of Chemistry, University of Bristol, Cantocks Close, Bristol, BS8 1TS, UK.

**Experimental**

- Synthesis of new complexes  
- Dehydrocoupling methodology  
- Selected $^{11}$\textsuperscript{B} NMR spectra  
  - Figure S-1  0.2 mol % 1b; Recycling experiment  
  - Figure S-2  0.2 mol % 1b; Filtration experiment

H$_3$B·NMe$_2$H Dehydrocoupling plots

- Figure S-3  5 mol % 1b  
- Figure S-4  5 mol % 1b; Hg experiment  
- Figure S-5  5 mol % 1b; Ph$_2$P(CH$_2$)$_3$PPh$_2$ experiment  
- Figure S-6  5 mol % 1b; PPh$_3$ experiment  
- Figure S-7  1 mol % 1b  
- Figure S-8  0.2 mol % 1b  
- Figure S-9  0.2 mol % 1c  
- Figure S-10  0.2 mol % 1d  
- Figure S-11  H$_3$B·NMe$_2$BH$_2$·NMe$_2$H experiment

Crystallography

- Table 1  Crystallographic data for 1b, 2b and 2d  
- Figure S-12  Solid state structure of 1b

References
Experimental

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk and glove-box techniques. Glassware was oven dried at 130°C overnight and flamed under vacuum prior to use. MeCN, THF, hexane and pentane were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles. \(^1\) CD\(_2\)Cl\(_2\), C\(_6\)H\(_5\)F and 1,2-C\(_6\)H\(_4\)F\(_2\) were distilled under vacuum from CaH\(_2\) and stored over 3 Å molecular sieves, 1,2-C\(_6\)H\(_4\)F\(_2\) was stirred over alumina for two hours prior to drying. H\(_3\)B·NMe\(_3\) and H\(_3\)B·NMe\(_2\)H were purchased from Aldrich and sublimed before use (5 × 10\(^{-2}\) Torr, 298 K). H\(_3\)B·NMeH\(_2\) \(^2\) and [Rh(NBD)(Ph\(_2\)P(CH\(_2\))\(_n\)PPh\(_2\))]\([\text{BARF}_4]\) (n=2-5) \(^3\) were prepared as previously described. NMR spectra were recorded on Varian Unity Plus 500 MHz or Varian Venus 300 MHz spectrometers at room temperature unless otherwise stated. In C\(_6\)H\(_5\)F, \(^1\)H NMR spectra were referenced to the centre of the downfield solvent multiplet (\(\delta = 7.11\)). \(^{31}\)P spectra were referenced against 85% H\(_3\)PO\(_4\) (external). \(^{11}\)B NMR spectra were referenced against BF\(_3\)·OEt\(_2\) (external). Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker MicrOTOF instrument. Microanalyses were performed by Elemental Microanalysis Ltd and London Metropolitan University. GPC data were obtained in THF solutions at 0.5 mg/ml, containing 0.1 % [nBu\(_4\)]NBr and use polystyrene standards for column calibration. Both the instrumentation and method are described in detail elsewhere. \(^4\)

Synthesis of new complexes

Preparation of [Rh(Ph\(_2\)P(CH\(_2\))\(_2\)PPh\(_2\))(C\(_6\)H\(_5\)F)][BARF\(_4\)] (1a)

A suspension of [Rh(Ph\(_2\)P(CH\(_2\))\(_2\)PPh\(_2\))Cl\(_2\)] \(_2\) (80.0 mg, 0.0745 mmol) and Na[BARF\(_4\)] (132.1 mg, 0.149 mmol) in C\(_6\)H\(_5\)F (10 mL) was stirred at room temperature for 2 hours. Pentane (8 mL) was added to the flask to encourage the full precipitation of NaCl (which is partially soluble in C\(_6\)H\(_5\)F) and then filtered. The product was isolated by first concentrating the filtrate (~ 5 mL) and then adding the solution dropwise to pentane (30 mL) with rigorous stirring causing 1a to precipitate as a red solid. Yield 80 mg, 37 %.

\(^1\)H NMR (500 MHz, C\(_6\)H\(_5\)F): \(\delta\) 8.37 (s, 8H, BAR\(_4\)), 7.63 (s, 4H, BAR\(_4\)), 1.83 (apparent d, \(J = 20\), 4H, CH\(_2\)). The co-ordinated C\(_6\)H\(_5\)F signals were not unambiguously located and the phenyl signals not assigned as they were obscured by C\(_6\)H\(_5\)F solvent \(\delta\) 7.31 – 6.70.

\(^{31}\)P {\(^1\)H} NMR (121 MHz, C\(_6\)H\(_5\)F): \(\delta\) 73.48 [d, \(J(\text{RhP}) = 203\)].

ESI-MS (C\(_6\)H\(_5\)F, 60°C, 4.5kV) positive ion: m/z, 597.1083 [M]+, (calc. 597.0778).

Anal. Calcd for C\(_6\)H\(_{11}\)B\(_1\)F\(_{26}\)P\(_2\)Rh\(_1\) (1460.6344 gmol\(^{-1}\)): C, 52.63; H, 2.83. Found: C, 52.17; H, 3.25.
Preparation of [Rh(Ph_2P(CH_2)_nPPh_2)(C_6H_5F)][BArF_4] n = 3 (1b), 4 (1c), 5 (1d).

In a typical experiment, [Rh(Ph_2P(CH_2)_nPPh_2)(NBD)][BArF_4] (100 mg) was stirred in C_6H_5F (5 mL) in a Young’s flask until fully dissolved. The flask was placed under hydrogen (4 atm) and then left to stir at room temperature for 20 minutes. The solution was then concentrated in vacuo (~2 mL) and then added dropwise to pentane (30 mL) with rigorous stirring resulting in the precipitation of 1b-d as a red/orange solid. Diffusion of pentane into a solution of the isolated solid in C_6H_5F (3 mL) gave 1b as red crystals. Yield: 74 mg, 74 % (1b), 72 mg, 72 % (1c), 78 mg, 78 % (1d).

1b

^1^H NMR (500 MHz, C_6H_5F): δ 8.37 (s, 8H, BArF_4), 7.65 (s, 4H, BArF_4), 5.66 (m, 4H, o&m-C_6H_5F), 5.08 (m, 1H, p-C_6H_5F), 2.06 (m, 4H, CH_2), 1.57 (m, 2H, CH_2). The phenyl signals were not assigned as they were obscured by C_6H_5F solvent δ 7.31 – 6.70.

^3^P (^1^H) NMR (202 MHz, C_6H_5F): δ 25.50 [d, J(RhP) 196].

ESI-MS (C_6H_5F, 60°C, 4.5kV) positive ion: m/z, 611.1351 [M]^+ (calc. 611.0935).

Anal. Calcd for C_{65}H_{43}B_1F_{25}P_2Rh_1 (1474.6610 gmol^-1): C, 52.94; H, 2.94. Found: C, 52.85; H, 2.47.

1c

^1^H NMR (500 MHz, C_6H_5F): δ 8.37 (s, 8H, BArF_4), 7.65 (s, 4H, BArF_4), 5.50 (m, 2H, o&m-C_6H_5F), 5.44 (m, 2H, o&m-C_6H_5F), 5.10 (m, 1H, p-C_6H_5F), 1.99 (m, 4H, CH_2), 1.24 (m, 2H, CH_2). The phenyl signals were not assigned as they were obscured by C_6H_5F solvent δ 7.31 – 6.70.

^3^P (^1^H) NMR (121 MHz, C_6H_5F): δ 38.39 [d, J(RhP) 199].

ESI-MS (C_6H_5F, 60°C, 4.5kV) positive ion: m/z, 625.1256 [M]^+ (calc. 625.1091).

Anal. Calcd for C_{66}H_{45}B_1F_{25}P_2Rh_1 (1488.6876 gmol^-1): C, 53.25; H, 3.05. Found: C, 53.28; H, 3.38.

1d

^1^H NMR (500 MHz, C_6H_5F): δ 8.37 (s, 8H, BArF_4), 7.65 (s, 4H, BArF_4), 5.54 (m, 2H, o&m-C_6H_5F), 5.49 (m, 2H, o&m-C_6H_5F), 5.26 (m, 1H, p-C_6H_5F), 2.11 (m, 2H, CH_2), 1.95 (m, 4H, CH_2), 1.59 (m, 4H, CH_2). The phenyl signals were not assigned as they were obscured by C_6H_5F solvent δ 7.31 – 6.70.

^3^P (^1^H) NMR (202 MHz, C_6H_5F): δ 27.01 [d, J(RhP) 207].

ESI-MS (C_6H_5F, 60°C, 4.5kV) positive ion: m/z, 639.1730 [M]^+ (calc. 639.1248).

Preparation of [Rh(Ph2P(CH2)3PPh2)(H3B·NMe3)][BArF4] (2b).

H3B·NMe3 (1.2 mg, 0.016 mmol) was added to a solution of 1b (24 mg, 0.016 mmol) in 1,2-C6H4F2 (3 mL). Diffusion of pentane at -35°C yielded 2b as red crystals. Yield: 14 mg, 59 %.

1H NMR (500 MHz, CD2Cl2): δ 7.74 (m, 8H, BArF4), 7.66 – 7.60 (m, 8H, Ph), 7.49 – 7.35 (m, 12H, Ph), 2.59 (s, 9H, NMe), 2.40 (m, 4H, CH2), 2.01 (m, 2H, CH2), -1.30 (br, 3H, BH3).

31P {1H} NMR (202 MHz, 1,2-C6H4F2): δ 34.02 [d, J(RhP) 167].

11B NMR (121 MHz, CD2Cl2): δ 16.40 (v br).

ESI-MS (1,2-C6H4F2, 60°C, 4.5kV) positive ion: m/z, 629.1168 [M-H 3B·NMe3+C6H4F2]+ (100 %, calc. 629.0840), 515.0861 [M-H3B·NMe3]+ (40 %, calc. 515.0559).

Preparation of [Rh(Ph2P(CH2)4PPh2)(H3B·NMe3)][BArF4] (2c).

H3B·NMe3 (1.2 mg, 0.016 mmol) was added to a solution of 1c (24 mg, 0.016 mmol) dissolved in 1,2-C6H4F2 (3 mL). Diffusion of pentane at -35°C yielded 2c as purple crystals. Yield: 19 mg, 80 %.

1H NMR (500 MHz, CD2Cl2): δ 7.74 (m, 8H, BArF4), 7.69 – 7.61 (m, 8H, Ph), 7.54 – 7.41 (m, 12H, Ph), 2.51 (s, 9H, NMe), 2.47 (m, 4H, CH2), 1.84 (m, 4H, CH2), -1.66 (br, 3H, BH3).

31P {1H} NMR (121 MHz, 1,2-C6H4F2): δ 47.12 [d, J(RhP) 170].

11B NMR (121 MHz, CD2Cl2): δ 18.26 (br).

ESI-MS (1,2-C6H4F2, 60°C, 4.5kV) positive ion: m/z, 643.1342 [M-H 3B·NMe3+C6H4F2]+ (100 %, calc. 643.0997), 602.2105 [M]+ (10 %, calc. 602.1784).

Preparation of [Rh(Ph2P(CH2)5PPh2)(H3B·NMe3)][BArF4] (2d).

H3B·NMe3 (1.2 mg, 0.016 mmol) was added to a solution of 1d (24 mg, 0.016 mmol) dissolved in 1,2-C6H4F2 (3 mL). Diffusion of pentane at -35°C yielded 2d as purple crystals. Yield: 21 mg, 89 %.

1H NMR (500 MHz, CD2Cl2): δ 7.74 (m, 8H, BArF4), 7.57 (m, 8H, Ph), 7.55 – 7.30 (m, 12H, Ph), 2.55 (s, 9H, NMe), 2.66 (m, 2H, CH2), 2.39 (m, 4H, CH2), 1.75 (m, 4H, CH2), -1.99 (br, 3H, BH3).

31P {1H} NMR (202 MHz, 1,2-C6H4F2): δ 34.89 [d, J(RhP) 176].

11B NMR (121 MHz, CD2Cl2): δ 20.34 (br).

ESI-MS (1,2-C6H4F2, 60°C, 4.5kV) positive ion: m/z, 657.0915 [M-H 3B·NMe3+C6H4F2]+ (100 %, calc. 657.1153), 616.1779 [M]+ (75 % calc. 616.1941).
Dehydrocoupling methodology

$\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ dehydrocoupling experiments for dehydrocoupling plots

A stock solution of $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ in 1,2-$\text{C}_6\text{H}_4\text{F}_2$ (0.07 M) was added to a Schlenk flask under argon containing the catalyst (1b-d) which was itself attached to an external mineral oil bubbler. 100 µL aliquots were taken over time; these were quenched immediately in an NMR tube by addition of MeCN (250 µL) and frozen to 77 K until analysis by $^{11}$B NMR Spectroscopy. $^{11}$B NMR spectra were processed using back linear prediction. Peaks which never reach > 10 % total integration value were not included in the analysis but are detailed in the footnotes of each plot.

$\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ polymerisation

To a Schlenk flask charged with catalyst (1b-d) and $\text{H}_3\text{B}\cdot\text{NMe}_2\text{H}$ (100 mg, 2.2 mmol) was added 1,2-$\text{C}_6\text{H}_4\text{F}_2$ (5 mL) and the resulting solution stirred open to argon for 2 hours. The reaction was subsequently quenched by addition of hexane (30 mL). After the precipitation of the polymer (ca. 10 minutes), the solvent was removed by decantation and the resulting solid redissolved in THF (3 mL). This solution was filtered into a new Schlenk containing hexane (30 mL). After decanting all solvent the resulting solid was dried overnight in vacuo. These polymerisations were essentially quantitative by $^{11}$B NMR spectroscopy, even though isolated yields are lower.

Isolated yields:
0.2 mol % 1b: 57 mg, 60 %
0.2 mol % 1c: 48 mg, 50 %
0.2 mol % 1d: 14 mg, 15 %
1 mol % 1b: 72 mg, 75 %
Selected $^{11}$B NMR spectra

Figure S-1: Representative $^{11}$B NMR spectra during catalyst recycling experiment. 500 eq. H$_3$B·NMe$_2$H in 1,2-C$_6$H$_4$F$_2$ (5 mL) added to 1b at t = 0 minutes. ‡ A further 500 eq. H$_3$B·NMe$_2$H (based on amount 1b remaining after 30 minutes of sampling) in 600 µL 1,2-C$_6$H$_4$F$_2$ added at 31 minutes. a = [H$_2$BNMe$_2$]$_2$, b = H$_3$B·NMe$_2$H.

Figure S-2: Representative $^{11}$B NMR spectra during catalyst filtration experiment to test for heterogeneous catalysis. Catalysis solution taken into glove box and filtered between 30 minutes and 66 minutes. ‡ 500 eq. H$_3$B·NMe$_2$H (based on amount of catalyst remaining after 30 minutes of sampling) in 600 µL 1,2-C$_6$H$_4$F$_2$ added at 66 minutes. a = [H$_2$BNMe$_2$]$_2$, b = H$_3$B·NMe$_2$H.
**H₃B·NMe₂H Dehydrocoupling plots**

![Graph showing dehydrocoupling plots for H₃B·NMe₂H](image)

**Figure S-3:** Representative plot of the catalytic dehydrocoupling of H₃B·NMe₂H (5 mol % 1b). Minor species observed by ¹¹B NMR Spectroscopy but not included in the above plot are: [H₂BNMe₂]₂ δ 28.6 (br d, J = 130) observed from 5 – 60 minutes, trace quantity remains at 60 minutes; H₃BNMe₂BH₂NMe₂H δ 2.5 (t, J = 108) -12.9 (q, J = 95) observed from 40 minutes, trace quantity remains at 60 minutes.

**Figure S-4:** Representative plot of the catalytic dehydrocoupling of H₃B·NMe₂H (5 mol % 1b). 100 µL Hg added by syringe to the catalytic mixture at 31 minutes (dotted line). Minor species observed by ¹¹B NMR Spectroscopy but not included in the above plot.
are: [HB(NMe2)] δ 28.6 (br d, J = 130) observed 10 - 70 minutes, trace quantity remains at 70 minutes; H3BNMe2BH2NMe2H δ 2.5 (t, J = 108) -12.9 (q, J = 95) observed from 35 minutes, trace quantity remains at 70 minutes.

Figure S-5: Representative plot of the catalytic dehydrocoupling of H3B·NMe2H (5 mol % 1b). 2 eq. Ph2P(CH2)2PPh2 in 600 µL 1,2-C6H4F2 added by syringe to the catalytic mixture at 31 minutes (dotted line). Minor species observed by 11B NMR Spectroscopy but not included in the above plot are: [HB(NMe2)] δ 28.6 (br d, J = 130) observed 5 – 60 minutes, trace amount remains at 60 minutes; H3BNMe2BH2NMe2H δ 2.5 (t, J = 108) -12.9 (q, J = 95) observed from 35 minutes, < 5% remains at 60 minutes.

Figure S-6: Representative plot of the catalytic dehydrocoupling of H3B·NMe2H (5 mol % 1b). 0.3 eq. PPh3 in 600 µL 1,2-C6H4F2 added by syringe to the catalytic mixture at 31 minutes (dotted line). Minor species observed by 11B NMR Spectroscopy but
not included in the above plot are: [HB(NMe2)2] δ 28.6 (br d, J = 130) observed 5 - 80 minutes; H3BNMe2BH2NMe2H δ 2.5 (t, J = 108) -12.9 (q, J = 95) observed from 35 minutes, < 5% remains at 60 minutes.

Figure S-7: Representative plot of the catalytic dehydrocoupling of H3B·NMe2H (1 mol % 1b). Minor species observed by 11B NMR Spectroscopy but not included in the above plot are: [HB(NMe2)2] δ 28.6 (br d, J = 130) observed from 12 - 30 minutes, trace quantity remains at 30 minutes. Dotted lines indicate the reduction of signals closer to the baseline resulting in reliable integration not being possible. Species at δ 0.5 (t, J = 103) and δ 0 (br) are observed from 12 - 20 minutes.

Figure S-8: Representative plot of the catalytic dehydrocoupling of H3B·NMe2H (0.2 mol % 1b). Minor species observed by 11B NMR Spectroscopy but not included in the above plot are: δ 19.4 (br) observed at 8 minutes and δ 3.5 (t, J = 117) observed from 10 -30 minutes, < 5% remains at 30 minutes. Dotted lines indicate the reduction of signals closer to the baseline resulting in reliable integration not being possible. Species at δ 0.5 (t, J = 103) and δ 0 (br) are observed from 2 - 25 minutes.
Figure S-9: Representative plot of the catalytic dehydrocoupling of H₃B·NMe₂H (0.2 mol % 1c). Minor species observed by $^{11}$B NMR Spectroscopy but not included in the above plot are: $\delta$ 19.4 (br) observed at from 5 – 100 minutes, trace quantity remains at 100 minutes; $\delta$ 3.5 (t, $J = 117$) observed from 20 -100 minutes, < 5 % remains at 100 minutes. Dotted lines indicate the reduction of signals closer to the baseline resulting in reliable integration not being possible. Species at $\delta$ 0.5 (t, $J = 103$) and $\delta$ 0 (br) are observed from 5 - 80 minutes.

Figure S-10: Representative plot of the catalytic dehydrocoupling of H₃B·NMe₂H (0.2 mol % 1d). Minor species observed by $^{11}$B NMR Spectroscopy but not included in the above plot are: $\delta$ 19.4 (br) observed from 20 - 240 minutes, < 5 % remains at 240 minutes and $\delta$ 3.5 (t, $J = 117$) observed from 20 - 240 minutes, < 5 % remains at 240 minutes. Dotted lines indicate the reduction of signals closer to the baseline resulting in reliable integration not being possible. Species at $\delta$ 0.5 (t, $J = 103$) and $\delta$ 0 (br) are observed from 20 - 240 minutes, trace quantity remains at 240 minutes.
Figure S-11: Representative $^{11}$B NMR spectra during $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H} + \text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ experiment. 50 eq. $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}$ in 1,2-C$_6$H$_4$F$_2$ (5 mL) added to $\text{1b}$ at $t = 0$ minutes. ‡ 400 eq. $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$ added to the reaction mixture at 33 minutes. a = $[\text{H}_2\text{BNMe}_2]^2$, b = $\text{H}_3\text{B} \cdot \text{NMe}_2\text{H}$, c = $\text{H}_3\text{B} \cdot \text{NMe}_2\text{BH}_2 \cdot \text{NMe}_2\text{H}$.
Crystallography

Relevant details about the structure refinements are given in Table 1. Data were collected on an Enraf Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a low-temperature device; data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK. The structures were solved by direct methods using SIR2004 (1b, 2d) or by Patterson interpretation using SHELXS-86 (2b) and refined full-matrix least squares on F² using SHELXL-97. All non-hydrogen atoms were refined anisotropically. H1A, H1B, H1C in 2d were located on the Fourier difference map; their isotropic displacement parameters were fixed to ride on the parent atoms. The following restraints were applied: B1-H1A = B1-H1B; H1A-H1C = H1B-H1C. H1A, H1B, H1C, H11A, H11B and H11C in 2b were placed in calculated positions, with the B-H distance free to refine (the restraint B1-H1A = B1-H1B = B1-H1C = B11-H11A = B11-H11B = B11-H11C was applied). All other hydrogen atoms were placed in calculated positions using the riding model. Disorder of the fluorobenzene ligand in 1b was treated by modelling the fluorine atom over three sites and restraining the 1,2- and 1,3- C-F distances. A planarity restraint was also applied about each disordered fluorine atom. Disorder of the amine-borane ligand in 2b was treated by modelling it over two sites and restraining its geometry. Problematic solvent disorder in the structure of 2b was treated using the SQUEEZE algorithm. Further details of disorder modelling are documented in the crystallographic information files under the heading _refine_special_details. Restraints to thermal parameters were applied where necessary in order to maintain sensible values.
Table 1: Crystallographic data for 1b, 2b and 2d.

<table>
<thead>
<tr>
<th></th>
<th>1b</th>
<th>2b.5/4(C(_6)H(_4)F(_2))</th>
<th>2d.(C(_6)H(_4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC number</td>
<td>801544</td>
<td>801541</td>
<td>801542</td>
</tr>
<tr>
<td>Formula</td>
<td>C(<em>{65})H(</em>{43})BF(_2)P(_2)Rh</td>
<td>C(<em>{69.5})H(</em>{55})B(<em>2)F(</em>{26.5})NP(_2)Rh</td>
<td>C(<em>{69})H(</em>{66})B(<em>2)F(</em>{24})NP(_2)Rh</td>
</tr>
<tr>
<td>(M)</td>
<td>1474.65</td>
<td>1594.11</td>
<td>1551.70</td>
</tr>
<tr>
<td>Space group</td>
<td>P(-1)</td>
<td>P(-1)</td>
<td>P(_2)/c</td>
</tr>
<tr>
<td>(T) [K]</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>(a) [Å]</td>
<td>12.5134(2)</td>
<td>12.9731(2)</td>
<td>14.94180(10)</td>
</tr>
<tr>
<td>(b) [Å]</td>
<td>13.5513(2)</td>
<td>17.4492(2)</td>
<td>19.2670(2)</td>
</tr>
<tr>
<td>(c) [Å]</td>
<td>19.5061(4)</td>
<td>18.3033(3)</td>
<td>25.1468(2)</td>
</tr>
<tr>
<td>(\alpha) [deg]</td>
<td>105.8393(7)</td>
<td>110.1373(6)</td>
<td>90</td>
</tr>
<tr>
<td>(\beta) [deg]</td>
<td>94.3128(7)</td>
<td>95.3780(7)</td>
<td>91.2143(3)</td>
</tr>
<tr>
<td>(\gamma) [deg]</td>
<td>94.6952(9)</td>
<td>99.4374(7)</td>
<td>90</td>
</tr>
<tr>
<td>(V) [Å(^3)]</td>
<td>3154.98(9)</td>
<td>3786.61(9)</td>
<td>7237.73(11)</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Density [gcm(^{-3})]</td>
<td>1.552</td>
<td>1.398</td>
<td>1.424</td>
</tr>
<tr>
<td>(\mu) (mm(^{-1}))</td>
<td>0.436</td>
<td>0.372</td>
<td>0.382</td>
</tr>
<tr>
<td>(\theta) range [deg]</td>
<td>5.14 (\leq) (\theta) (\leq) 26.37</td>
<td>5.50 (\leq) (\theta) (\leq) 26.37</td>
<td>5.11 (\leq) (\theta) (\leq) 26.37</td>
</tr>
<tr>
<td>Reflns collected</td>
<td>19313</td>
<td>26357</td>
<td>28480</td>
</tr>
<tr>
<td>(R_{cr})</td>
<td>0.0246</td>
<td>0.0216</td>
<td>0.0224</td>
</tr>
<tr>
<td>Completeness</td>
<td>98.0 %</td>
<td>98.3 %</td>
<td>99.2 %</td>
</tr>
<tr>
<td>No. of data/restr/param</td>
<td>12382 / 654 / 1005</td>
<td>15201 / 1668 / 1196</td>
<td>14685 / 542 / 1018</td>
</tr>
<tr>
<td>(R_1) ([I &gt; 2\sigma(I)])</td>
<td>0.0458</td>
<td>0.0529</td>
<td>0.0427</td>
</tr>
<tr>
<td>(wR_2) [all data]</td>
<td>0.1145</td>
<td>0.1541</td>
<td>0.1072</td>
</tr>
<tr>
<td>GoF</td>
<td>1.020</td>
<td>1.046</td>
<td>1.025</td>
</tr>
<tr>
<td>Largest diff. pk and hole [eÅ(^{-3})]</td>
<td>0.622, -0.545</td>
<td>0.840, -0.604</td>
<td>0.663, -0.405</td>
</tr>
</tbody>
</table>
Figure S-12  Solid state structure of 1b; ellipsoids drawn are depicted at the 50% probability level. Anion and minor disordered components omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1-P1, 2.2266(9); Rh1-P2 2.2343(9); Rh1-C_{arene}, 2.292(4) – 2.377(4), P1-Rh1-P2 90.07(3).
References


